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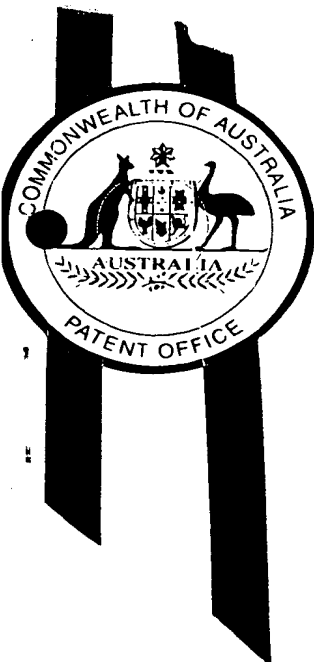
I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 9894 for a patent by VINPAC INTERNATIONAL PTY LTD filed on 22 April 1999.

WITNESS my hand this  
Tenth day of May 2000

*K Ward*

KAY WARD  
TEAM LEADER EXAMINATION  
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VINPAC INTERNATIONAL PTY LTD

**ORIGINAL**

AUSTRALIA  
PATENTS ACT 1990

PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

"TREATED CLOSURES 3"

This invention is described in the following statement:

## BACKGROUND TO THE INVENTION

This invention relates to improved closures for use in connection with food or beverages. One application is in relation to improved closures for wine bottles.

5 Wine bottles have traditionally been stoppered with corks made from natural cork material. However, this material can be subject to initial flaws, or deteriorate in use, resulting in contamination or spoilage of the wine. For example, oxidation of the wine, due to permeation of oxygen through the cork into the wine, results in vinegar flavour. "Cork taint", due to the presence of trichloro-anisoles (TCA) and other  
10 flavour active compounds in the cork, imparts a musty or mouldy smell and flavour to the wine. Leakage can also be a problem. Furthermore, cork is a relatively expensive material, as most supplies still come from Portugal.

15 None of the alternatives to natural corks proposed to date have been entirely satisfactory.

Plastic stoppers and screw-cap stoppers may be as effective as natural corks, but have not yet been tested adequately over the prolonged storage periods of quality red wines. Furthermore, there is considerable consumer resistance to use of such  
20 stoppers, particularly for quality wines.

Accordingly, there have been numerous attempts to improve on natural cork stoppers, by coating or impregnating them.

25 The first cork coatings were simply lubricants such as paraffin and Vaseline. These merely ensured that the cork was easier to insert into the bottle and later remove, without disintegration. The other problems associated with cork stoppers were not addressed. Furthermore, the compounds used as lubricants generally tend to melt under conditions necessary for pasteurisation (50-100° C).

30 Currently, materials used in surface treatment of corks include oils and silicone resins, emulsions of various formulations, as well as some plastic coatings. These

coatings do prevent leakage of the wine, but do not provide a barrier against taint and oxidation.

5 Many of these coatings also present problems with the coating coming off the cork and leaving an oily layer on the wine surface.

10 Hybrid corks have been moulded from natural cork and synthetic cork cells made from a plastic polymer. The synthetic cells fill the gaps between the cork cells, and a binding agent (such as polyurethane) is used to bind the cells together. However, hybrid corks have to date proved unsatisfactory, as they often leak and can disintegrate and be difficult to extract from a bottle.

15 The present invention provides an improved closure having a surface coating or diffusion layer comprising an appropriate polymer. This coating or diffusion layer has many properties which are of benefit when used (for example) in relation to corks for wine bottles. The coating or diffusion layer limits oxygen permeability, inhibits or prevents the diffusion of trichloro-anisoles (TCA) and other flavour active compounds into the wine, adheres strongly to the cork and/or penetrates into the surface of the cork, is sufficiently flexible to be capable of withstanding compression and decompression during the corking process, enables the coated cork to be readily extracted from the bottle, reduces or prevents wine leakage, is resistant to sulphur dioxide, has long life under ethanolic conditions, and is acceptable to the food and beverage industry with respect to toxicology (ie it is non-toxic or does not leach into the wine).

25 These coatings or diffusion layers are also applicable to substrates other than cork (eg packaging and wrapping materials) which are directly or indirectly in contact with food products or beverages.

## 30 SUMMARY OF THE INVENTION

According to the present invention, a copolymer comprising a flexible polymer attached to a rigid block polymer compound is applied as a surface coating or

diffusion layer to a substrate for use in direct or indirect contact with food products or beverages. The flexible component of the copolymer may be silicon-based, but the copolymers of the present invention are not restricted to those comprising silicon-based monomers. Other flexible monomers providing the necessary requirements for the coating may also be used.

The substrate may, for example, be a bottle closure (such as a cork), packaging and wrapping materials (such as packaging for cheese), or a bottle or other container.

As mentioned above, the copolymer comprises a flexible (eg silicon-based) polymer attached to a block polymer compound (which does not flex). This multi-component polymer structure acts as a partial physical barrier to the passage of gases and flavour active compounds, whilst having the physical properties (in particular, flexibility) required during the treatment and packaging processes. The copolymer is also selected for other advantageous properties, such as adhering strongly to the substrate and/or penetrating into the surface of the substrate, and being acceptable to the food and beverage industry with respect to toxicology (ie being non-toxic or not leaching into the food product or beverage). Furthermore, if the substrate is a cork, the copolymer coating or diffusion layer must enable the coated cork to be readily extracted from the bottle, prevent wine leakage, and have long life under ethanolic conditions. Preferably, the copolymer coating or diffusion layer will also be resistant to sulphur dioxide and changes in pH.

#### DETAILED DESCRIPTION OF THE INVENTION

The copolymers of the present invention may be graft, alternating or block copolymers. Suitable copolymers are described in the following references:

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Examples of such copolymers are:

polyvinylacetate (PVA) copolymers

polyurethane copolymers and ionomers

terephthalate copolymers

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styrene-acrylonitrile (SAN)/acrylonitrile-butadiene-styrene (ABS) copolymers  
(vinylidene) copolymers

epoxy copolymers

amide copolymers

Bisphenol copolymers

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Bisphenol A (BPA) - epichlorohydrin

poly (methyl) methacrylate and copolymers

poly (methacrylic acid) copolymers

cellulose copolymers

25 siloxane copolymers, eg comprising polyethylene glycol (PEG), isoprene,  
butadiene, lactone, amino, terephthalate, amino acid, heterocyclic, hydride (SiH) or  
epoxy functionalities

PVA and functionalised siloxanes (eg comprising SiH or amino groups) have been found to be particularly suitable components of the copolymers.

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Modifications of the polymers may be necessary to improve resistance to reactions with various components of the food product or beverage (eg wine).

The method of applying the copolymer to the substrate will be dependent on the nature of the copolymer and of the substrate, and will include such conventional processes as film formation, adsorption from solution, reactive-adhesion to cork, melt polymer application (eg thermoforming, vacuum forming and plasma

5 polymerisation), UV curing and Corona discharge processes. The polymers may also be components of multi-layer laminate structures.

Preferably, the substrate (eg cork) is prewashed with a solution (eg ethanol, water or a mixture of ethanol and water) and then dried before coating, to remove any surface  
10 contamination.

The following examples form an overview of some of the technologies which may be used. These examples are illustrative, but not restrictive, of the present invention.

## 15 SYNTHESIS OF COPOLYMERS

### EXAMPLES:

#### Hydrosilylation of Polybutadiene

A mixture of polybutadiene ( $M_n = 400$ , 9.1g, 0.023mol), triethoxysilane (4.2g,  
20 25mmol),  $H_2PtCl_6$  (0.8ml) in toluene, was refluxed for 24 hours under nitrogen at  $110^\circ C$ . The solution was then allowed to cool, and solvent and excess triethoxysilane was evaporated under vacuum to give a pale yellow oil as a product. The product was confirmed by  $^1H$  nmr.

#### 25 Hydrosilylation of Polyisoprene

The reduction of Ni(acetylacetonate) (78mg, 0.3mmol) in polyisoprene ( $M_n = 800,000$ , 12.0g, 0.015mmol) with  $AlEt_3$  (0.6mmol in 0.6 mol hexane) was carried out anaerobically, using an ice bath for cooling. After addition of triethoxysilane (4.2g, 25mmol), the mixture was set aside at room temperature. The reaction mixture was  
30 then evaporated to remove excess triethoxysilane and solvent to give the product, which was confirmed by  $^1H$  nmr.

### Hydrosilylation of Polyethylene Glycol Methyl Ether

- A mixture of the polyethylene glycol methyl ether (5.5g, 16mmol), allyl bromide (3.5g, 29mmol), sodium hydroxide pellets (1.2g, 30mmol) and n-hexane (6ml) was
- 5    refluxed at 66°C for 17 hours and was allowed to cool. Solvent and the non-reacted allyl bromide was evaporated under vacuo, diluted with isobutyl alcohol, washed with water (x3), brine, and the solvent evaporated to give a yellow-brown liquid. FTIR was used to confirm the product as allyl polyethylene glycol methyl ether.
- 10    The allyl ether (2.2g) in a mixture of triethoxysilane (0.98g, 6.0mmol),  $\text{H}_2\text{PtCl}_6$  (0.3ml) and THF (10ml) was refluxed overnight under nitrogen to give triethoxysilane-polyethylene glycol methyl ether polymer, which was confirmed by  $^1\text{H}$  nmr.

### TESTING OF COATINGS

- 15    Corks were deliberately spiked with TCA and coated with the coating as described in the procedure below. Tests were then performed to see if the TCA will penetrate through the new coating.

#### Procedure

- 20    The cork was immersed in a solution of 0.1M TCA in absolute alcohol for 24 hours after which it was removed from the solution and dried in an oven at 40°C for another 24 hours. The cork may then be rinsed with a solvent that can dissolve TCA and other off flavoured compounds, eg absolute ethanol or xylene, to remove any excess TCA that may have crystallised on the surface. The cork is then dried in the
- 25    oven again at 40°C for 24 hours. The cork is now ready for coating.

### METHODS OF APPLICATION

#### Dip Coating

- 30    The simplest application method is dip coating, involving a container filled with the coating formulation into which the substrate (such as a cork) is immersed and then withdrawn.



A typical dip coating unit consists of a bath, filled with the coating formulation, and a mechanism on which the substrate is mounted for immersion and withdrawal. It is often necessary to circulate and filter the coating to maintain a homogeneous mixture. A fixing mechanism must be designed to ensure the proper orientation of the substrate during immersion into and withdrawal from the fluid.

### **Spray Coating**

In contrast to dip coating, spray coating operations are much less efficient and much more complicated, as well as being relatively more expensive. Precise control over the spray area is difficult so that masking of the substrate may be required. The advantages offered by these systems (eg fast application time, very uniform coating thicknesses, and the ability to apply uniform coatings to irregularly shaped objects) may, however, outweigh the drawbacks.

In a spray coating operation, the fluid is atomised into fine droplets for application to the substrate. The size of the droplets formed during atomisation can be controlled by such properties as fluid flow, fluid pressure, air pressure, solution viscosity, and surface tension. A number of different nozzle designs are used in industry, such as compressed air spray nozzles, airless spray nozzles, and hot spray systems.

### **Slot and Curtain Coating**

Slot coating and curtain coating are more appropriate techniques for a continuous operation. The methods involve a stationary die, which delivers a layer of coating onto a substrate moving beneath it. The difference between the methods is in the way that the coating is transferred from the die to the moving substrate. The coating is spread by the slot method when the die slot is close to the substrate; but changing the orientation of the die slot relative to the conveyor and allowing the formulation to cascade is referred to as curtain coating.

Multiple slots in the die face or converging feed to a single slot can produce multilayer coatings.

### **Roll Coating**

Roll coating is another method used in continuous manufacturing operations primarily for coating films. A substrate is fed between two rotating cylinders, while simultaneously directing the coating into the space between the cylinders.

Formulation viscosity, speed of the substrate, coating flow rate, and distance between the rolls all contribute to coating thickness and uniformity. Although these systems are limited in the types of substrate that can be coated, they can rapidly produce a very uniform product.

## **METHODS OF CURING**

### **Thermal Cure**

One of the most common methods for initiating the cross-linking of a polymer is by heating, and ovens can be incorporated into batch and continuous-mode systems.

The main disadvantage in thermal curing is the wasted thermal energy when only a small amount of the applied energy is transferred to the molecules. It can also be difficult to maintain a uniform temperature throughout the oven, so that curing may be uneven.

### **Ultraviolet (UV) Cure**

One of the most popular techniques used to initiate cross-linking is irradiation by ultraviolet light. It can be a more rapid process than thermal curing, sometimes taking less than a second to act. Very little heat is generated during the exposure, which can often be carried out at room temperature.

### **Electron Beam Cure**

Electron beam (e-beam) radiation shares the same benefits as UV radiation, without the need for a photoinitiation. The exposure forms free radicals that cause the chain reaction.

### **Gamma-Radiation Cure**

Yet another type of irradiation that is rapid at ambient temperatures is  $\gamma$ -radiation cure. Cycle times for  $\gamma$ -ray systems can be longer than for e-beam, at least for conventional polymer matrices, but for curing hydrophilic coatings this does not present a problem.

## **ADDITIONAL TECHNOLOGIES**

### **Plasma Polymerisation**

Thin polymer films can be deposited onto various substrates through the use of plasma polymerisation. A plasma is generated by means of electron excitation, with a gas mixture and an organic monomer. These thin films can be between a few hundred angstroms to a micrometre in thickness. Cross-linking density is usually greater than in conventionally applied coatings, and thin films exhibiting good adhesion can be laid down on virtually any type of substrate.

### **Surface Grafting**

Surface grafting techniques incorporate some of the same general concepts as coating and curing operations but may be more appropriate where exceptionally thin surface layers are desired. Points that distinguish surface grafting from "wet" coating operations are related mainly to the formation of the modified surface layer and the general molecular structures that result. In conventional coatings, a continuous phase is formed by the reactions of the monomeric or polymeric ingredients, and is adhered to the substrate surface through secondary molecular interactions such as hydrogen bonding, london dispersive forces or acid-base interactions. Primary covalent bonding is also possible if the substrate has been pre-treated with molecular groups. In surface grafting however, the monomeric (or polymeric with reactive end groups) components react directly with a polymeric substrate. Various forms of radiation, such as UV, electron beam, and  $\gamma$ -rays, are used to cause the formation of peroxide groups on the polymer surface. These are unstable so decompose, and cause initiation of polymerisation in the process.

While the present invention has been described in terms of preferred embodiments in order to facilitate better understanding of the invention, it should be appreciated that various modifications can be made without departing from the principles of the invention. Therefore, the invention should be understood to include all such  
5 modifications within its scope.

Dated this 22<sup>nd</sup> day of April 1999.

10 VINPAC INTERNATIONAL PTY LTD  
By its Patent Attorneys  
MADDERNS



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